Studies on the Flame Spectrochemical Analysis. IV : Rapid Determinations of Calcium and Magnesium in Basic Slags

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Rapid Determinations of Calcium and Magnesium in Basic Slags*

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Synopsis

The rapid determinations of calcium and magnesium in basic blast furnace slags were studied by flame spectrochemical method and the factors influencing the flame emission of calcium or magnesium were also researched. Aluminium and phosphorus were main elements which interfered with the determination of calcium, while aluminium and calcium interfered with the magnesium determination. These influences were all avoided by adding them to the sample solutions to become their concentrations to be in definite ranges. After these researches, the rapid methods for the determination of calcium and magnesium in basic slag were established.

I. Introduction

The rapid determinations of calcium oxide and magnesium oxide in basic slags are appreciably difficult, although they are the serious problems in routine work in factory. Especially, the chemical analysis of magnesium is very complicated and time-consuming. Recently, however, the flame spectrophotometric method was developed for the determinations of calcium and magnesium and some results were reported, for example, in plant[1], water[2] or rocks[3]. As basic slag is very complicated in its chemical composition, there are many factors which affect the flame emissions of calcium or magnesium. So, it is necessary to standardize the condition for the determination of them by the flame spectrophotometric method. In the present research, various factors influencing the flame emissions of calcium and magnesium were examined and then the methods for the determination of calcium oxide and magnesium oxide contents in slags were established.

II. Experiments and results

1. Reagent and instrument

The standard solutions of calcium and magnesium were prepared respectively from calcium carbonate and magnesium oxide (Kahlbaum reagent, "Zur Analyse" grade) and acidified them 0.01N with HCl. Two calcium stock solutions were made: 1 mg/ml of Ca and 10 mg/ml of Ca. Magnesium solution was 1 mg/ml Mg. These solutions were diluted to a favorable concentration when they were used.

* The 831st report of Research Institute for Iron, Steel and Other Metals. Read at the 2nd Annual meeting of Japan Anal. Chem. Soc. Oct., 1953.

(1) O. N. Hinsverk, S. H. Wittmer and H.M. Sell, Anal. Chem., **25** (1953), 320.
(2) W. M. Plose, E. Smith and M. T. Watson, ibid., **25** (1953), 1023.
(3) E. J. Bird, R. E. Mosher and A. J. Boyle, ibid., **22** (1950), 715.

Aluminium solution was prepared by dissolving highly pure aluminium metal (99.9 per cent) with hydrochloric acid. Instruments used for the flame excitation and its intensity measurement were Beckman model DU spectrophotometer with the flame attachment of the type 9200.

2. Determination of calcium

(i) Concentration of calcium and conditions for emission measurement

The pressures of gases were fixed to 3 lb/in^2 for H_2 and 25 lb/in^2 for O_2. Calcium emission spectrum intensity was measured at 554 mμ. As the percentage of calcium content in usual basic slag was appreciably high, it was necessary to prepare the sample solution of suitable dilution. But, on the other side, slag contained various elements such as aluminium which weakened the flame intensity. Considering these circumstances, the experiment was proceeded by controlling the emission intensity of 75 γ/ml Ca to 50 per cent of scale reading with 0.2 mm slit width. This concentration agreed with 42 per cent calcium oxide in slags when 0.5 g of sample was dissolved in 100 ml, 25 ml which was finally diluted to 500 ml.

(ii) Influences of diverse elements

In general, aluminium extremely depresses the flame emission of metal elements[4,5] and affects also remarkably the calcium spectrum line as shown in Fig. 1. When aluminium concentration became above 20 γ/ml, however, the decrease in the intensity due to the change in aluminium concentration became slow, and above 50 γ/ml, it became independent of aluminium concentration. Then, by adding aluminium to the solution to become its final concentration above 50 γ/ml, the fluctuation of the calcium emission caused by aluminium could be avoided. Other elements, such as iron and manganese, had no influence till their concentration became 30 γ/ml. Phosphorus accompanying with aluminium, depressed the calcium emission when its concentration became higher than 5 γ/ml. As phosphorus content in basic slag is usually less than 5 per cent, phophorus interference conld be controlled within -1 per cent with the above sample concentration.

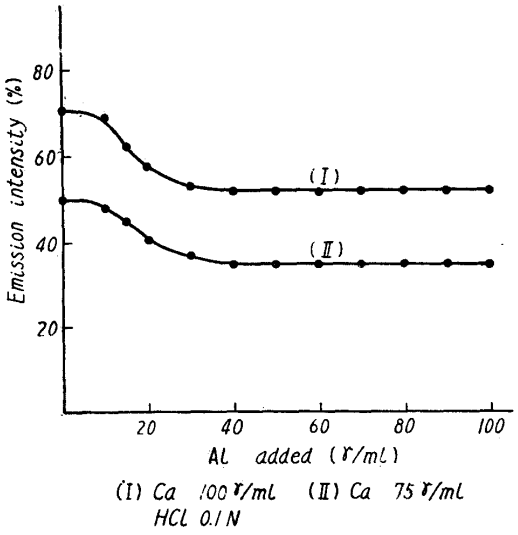


Fig. 1. Influences of aluminium on calcium emission.

Though silicate in slags was dissolved by hydrochloric acid, calcium was made by two procedures, one being treated after silicate separation and the other without any separation, but no difference was observable between them as shown in Table 4. From these results, it was assumed that silicate did not afiect the calcium determination.

(4) S. Ikeda, J. Chem. Soc., **76** (1955), 6.
(5) E. E. Strange, Anal. Chem., **25** (1953), 650.

Table 1. Influences of diverse elements on the calcium emission.

Elements added γ/ml	Ca 75 γ/ml			Ca 100 γ/ml		
	Fe	Mn	P	Fe	Mn	P
1	—	—	−0.3	—	—	−0.4
3	—	—	−0.7	—	—	−0.8
5	—	—	−2.2	—	—	−2.5
10	−0.3	−0.1	−9.6	−0.2	−0.1	−9.0
20	−0.8	−0.3	−24.6	−0.6	−0.3	−22.8
30	−1.0	−0.6	—	−0.8	−0.5	—
40	−1.2	−1.0	—	−1.4	−0.9	—
50	−1.6	−1.4	—	−1.8	−1.4	—

Table shows the decreasing rate of intensity.

(iii) The concentration of acid

When 50 γ/ml of aluminium and 75 γ/ml of calcium was contained in the solution hydrochloric acid, nitric acid or sulfuric acid of various concentrations were added and the change in the emission intensity was observed. As shown in Fig. 2, hydrochloric acid caused no change, while 0.05N of nitric acid or sulfuric acid depressed the intensity remarkably, but over 0.05N, the intensity became stable in both cases. Calcium or magnesium compounds in basic slag would be dissolved completely by hydrochloric acid, and so hydrochloric acid was adopted as the most suitable acid for the dissolution of slag sample. When nitric acid was used, the final acid concentration of solution of solution must be kept above 0.05N to avoid the emission fluctuation.

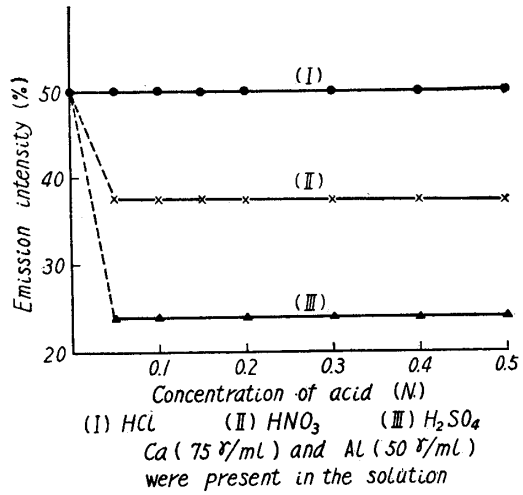


Fig. 2. Influences of acids on the calcium emission.

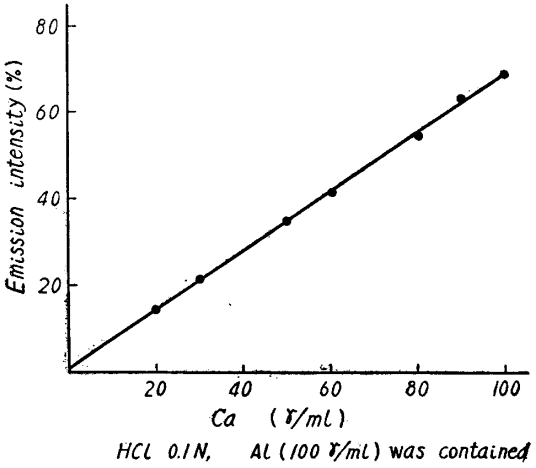


Fig. 3. Calibration curve for calcium.

(iv) The calibration curve of calcium

In the solution containing 100 γ/ml of aluminium, various amounts of calcium were added and hydrochloric acid concentration was kept to 0.1N, and then the relation between the emission intensity of the solution and calcium content was researched. In the range 1～100 γ/ml of calcium concentration, the proportionality was obtained between them as shown in Fig. 3, in which the mean value of five measurements was plotted, the deviation being only within ±0.08 per cent.

(v) Procedure of the analysis of calcium

From these results, the procedure for the rapid determination of calcium in slag was established as follows: 0.5 g of sample was dissolved with 30 ml of hydrochloric acid solution (1 : 1) and its volume was made 100 ml. 25 ml of this solution was taken (the residual solution was used for the determination of magnesium) and aluminium solution (containing 25 g of aluminium) was added to it, and then total volume was made 500 ml. Using this solution, calcium was emitted and its intensity was measured at 554 mμ, and then from the calibration curve previously obtained with standard solution containing as much aluminium as sample solution, calcium amount was determined. Calcium oxide content in slag could be calculated from the following formula:

$$CaO\ \% = 0.28\ C/S$$

C; Calcium amount obtained from calibration curve. (γ/ml)

S; Sample taken (g)

3. Determination of magnesium

(i) Concentration of magnesium and condition for flame emission

The percentage of magnesium concentration in basic slags was low, compared with that of calcium, the order being of several percent, and in addition there were large amounts of calcium in slags. So the intensity measurement was made by using the wave length of 371 mμ and the condition was fixed as follows: H_2 pressure was 4 lb/in^2 and O_2 pressure 30 lb/in^2. Wave length measured was 371 mμ and slit width was 0.4 mm. The emission intensity of magnesium solution containing 120 γ/ml of magnesium was adjusted to the scale reading of 60 per cent. This magnesium concentration corresponds to 4 per cent of magnesium oxide, when 0.5 g of slag sample was dissolved in 100 ml.

(ii) The concentration of acid

In the same way as in calcium emission, the magnesium intensity was decreased by the presence of nitric acid or sulfuric acid over 0.1N, but hydrochloric acid didn't cause any change in the concentration between 0~2N. So, hydrochloric acid could be assumed to be the most suitable acid in the determination of magnesium, too.

(iii) Influences of diverse elements

Next experiment was carried out on the behavior of magnesium emission and flame background at 371 mμ in the presence of various ions which were expected to be present in basic slag. The results are shown in Table 2, from which it will be seen that magnesium emission does not fluctuate in the presence of 1.3~1.5 g/ml of calcium and 300~1000 γ/ml of aluminium. Although phosphorus itself also decreased the magnesium emission, no influence was found at the concentration less than 150 γ/ml in the presence of appreciable amounts of calcium and aluminium. Over this concentration of phosphorus, however, a decreasing in emission appeared and lower results were obtained. Iron and manganese had no influence in the

usual concentration range in slag.

Silicic acid had not also any influence (see Table 4). As calcium, however, exists in large amounts, it affects the background at 371 mμ remarkably. Other elements within the concentration ranges discussed above (aluminium less than 1 mg/ml, phosphorus less than 200 γ/ml and iron and manganese less than 100 γ/ml) did not cause any background change. On the other hand, aluminium and phosphorus depress severely calcium emission, and so the experiments were carried out to research the intensity change of background at 371 mμ by keeping calcium content constant and varying the concentrations of aluminium or phosphorus. When the aluminium concentration was over 300 γ/ml and phosphorus concentration over 100 γ/ml, the background intensity did not reveal any variation. The behavior was the same even in the presence of other elements such as iron or manganese.

When the calcium concentration was varied, the intensity of background at 371 mμ varied in proportion to the increase in calcium in the solution. (Table 2)

Table 2. Influences of diverse elements on the magnesium emision.

Elements added			Intensity reading %	
Ca mg/ml	Al γ/ml	P γ/ml	Mg 120 γ/ml	Mg none
1.2	500	—	56.4	17.3
1.3	"	—	57.8	18.8
1.4	"	—	59.2	20.3
1.5	"	—	60.0	21.5
1.7	"	—	61.0	23.6
1.5	200	—	63.8	21.0
"	300	—	60.5	21.4
"	700	—	60.0	21.2
"	1000	—	60.0	21.4
"	1200	—	57.4	21.3
1.5	500	10	60.0	21.2
"	"	50	60.2	21.0
"	"	100	59.7	21.0
"	"	150	59.2	20.5
"	"	170	58.8	20.8
"	"	200	58.2	21.0
Ca 1.5 mg/ml, Al 500 γ/ml Fe, Mn 100 γ/ml,			60.6	21.8

Intensity readings listed were obtained by controlling the instrument to indicate the intensity of the solution composed of Ca 1.5 mg/ml, Al 500 γ/ml and magnesium 120 γ/ml to be 60% at 371 mμ.

(iv) Calibration of background and calibration curve of magnesium

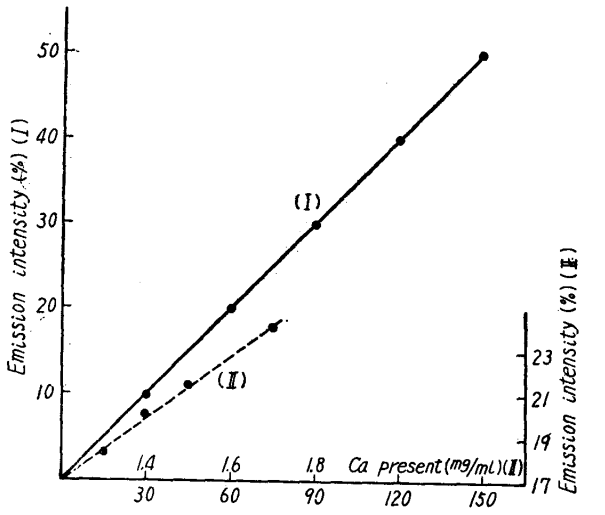
From the above result, it was found that only calcium affected the background intensity at 371 mμ, and that other elements assumed to be present in slag did not give any influence, so long as they were kept in the definite concentration range. Using two kinds of solutions, one containing magnesium, aluminium and calcium and the other not containing magnesium but aluminium and calcium, flame emission intensities at the wave lengths near 371 mμ were measured, respectively. As shown in Table 3, the magnesium emission was detected between 367 and 385 mμ with

Table 3. Change of magnesium intensity and background at the wave length near 371 mμ.

Wave length mμ	Mg 120 γ/ml	Mg none	Wave length mμ	Mg 120 γ/ml	Mg none
365	20.8	21.0	380	58.1	21.8
367	42.3	21.0	383	58.6	22.1
371	60.0	21.2	385	46.2	24.8
373	58.3	21.0	390	26.3	26.8
376	57.0	21.6			

Ca 1.5 mg/ml, Al 500 γ/ml were present. The table shows the intensity reading (%).

the slit width of 0.4 mm. At 365 mμ, however, the magnesium emission could not observed and the emission of the solution not containing magnesium, that is, the background intensity did not vary its intensity at 365~371 mμ. From these, the background could be calibrated by applying either method of the following two; (1) The intensity of sample solution was measured first at 371 mμ and next at 361 mμ. Then the magnesium intensity could be obtained from their difference. (2) By using the relation between the background and the calcium content obtained in the preliminary experiment, the background intensity at 371 mμ was calibrated from the calcium content previously determined, and subtracted from the intensity of sample solution and then the true magnesium intensity could be obtained from it. In Fig. 4, the calibration curve of magnesium and the background calibration curve against calcium content are shown and the calibrated results of magnesium intensity applying each method described above are listed in Table 4. It shows a good agreement with the deviation less than ±1 per cent.



(I) Calibration curve of magnesium HCl 2N, Ca (1.5 mg/ml) and Al (500 γ/ml) were present.
(II) Calibration curve for calcium background at 371 mμ. HCl 2N, Al (500 γ/ml) was present.

Fig. 4. Calibration curve for magnesium and calcium background at 371 mμ.

Table 4. Results of background calibration for magnesim emission.

Mg γ/ml	Intensity Calibrated (I) %	σ %	Intensity Calibrated (II) %	σ %
90	29.6	±0.12	29.8	±0.18
120	39.8	±0.16	39.2	±0.18
150	48.6	±0.15	48.4	±0.20

(1) Magnesium intensity was calibrated by subtracting the emission intensity at 365 mμ.
(2) Magnesium intensity was calibrated from calcium contents.

(v) Procedure for the determination of magnesium in slags

From these fundamental researches, the method for the determination of magnesium in slag was established as follows: 0.5 g of sample was dissolved in 30 ml of hydrochloric acid (1:1) and then the volume was made 100 ml. (This sample solution allowed to keep aluminium between from 300 γ/ml to 1 mg/ml and calcium between 1.2~1.7 mg/ml in the solution.) Using this solution the emission intensity was measured at 371 mμ and the background intensity, which was obtained by the emission of 365 mμ or by calibrated results from calcium cotents, was subtracted from it. With these calibrated results, magnesium was determined from the calibration curve previously given and then magnesium oxide could be obtained by the following formula:

$$MgO\ \% = 1/60 \times C/S$$

C; Magnesium amount determined (γ/ml)

S; Sample taken (g)

4. Determinations of calcium and magnesium in blast furnace slag

Applying these methods, the determinations of calcium and magnesium in several blast furnace slag samples were carried out and results obtained are shown in Table 5. The time required for the analysis of two elements in one sample was less than 15 min.

Table 5. Determination of CaO and MgO in blast furnace slag.

CaO % chemical analysis	CaO % determined	diff %	MgO % chemical analysis	MgO % determined	diff %
46.0	45.7	−0.3	3.30	3.51	+0.2
44.5	44.9	+0.4	5.00	5.40	+0.4
45.1	45.5	−0.4	3.62	3.60	−0.02
,,	* 45.0	−0.1	,,	* 3.65	+0.03
40.8	39.5	−1.3	4.02	4.32	+0.28
,,	* 39.0	−1.8	,,	* 4.22	+0.22

* Determined after the separation of silicic acid.

Summary

(1) The studies were carried out to determine rapidly calcium and magnesium in basic slag by using flame spectrochemical analysis.

(2) The flame emission of calcium was measured at 554 mμ and that of magnesium at 371 mμ.

(3) Hydrochloric acid was most suitable for dissolving the sample because of its none interference with flame emission of calcium or magnesium. But nitric acid and sulfuric acid decreased the emission to some definite extent.

(4) Aluminium and phosphorus higher than 5 γ/ml depress calcium intensity but these effects could be avoided by adding more aluminium than 50 γ/ml. Other element in the concentration ranges expected to be present in slag had no influence on calcium emission.

(5) The fluctation of magnesium flame intensity could be avoided by keeping the aluminium concentration in the solution to be 300 γ~1 mg/ml and calcium concentration 1.2~1.7 mg/ml.
(6) Background appeared on the magnesium intensity measurement at 371 mμ was calibrated by the emission at 365 mμ or by the calibration obtained from calcium content.
(7) By using these results, rapid determinations of calcium and magnesium in slag were established.

The present author expresses his hearty thanks to Prof. Hidehiro Gotô for his kindful guidance in the course of this work.